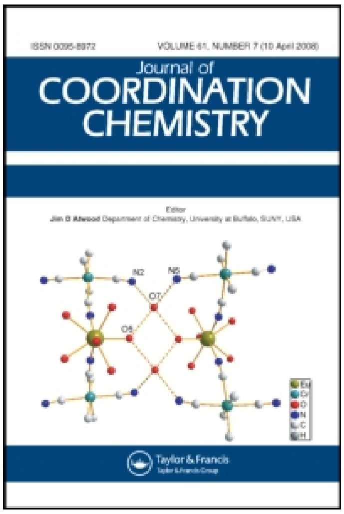

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Wenz, G. , Buschmann, H. J. and Schollmeyer, E.(1999) 'THERMODYNAMICS OF COMPLEXATION OF SOME MONOVALENT AND BIVALENT CATIONS BY CROWN ETHERS, BENZO CROWN ETHERS AND CRYPTANDS IN N,N-DIMETHYLFORMAMIDE', Journal of Coordination Chemistry, 48: 4, 465 — 476
To link to this Article: DOI: 10.1080/00958979908023586
URL: http://dx.doi.org/10.1080/00958979908023586

J. Coord. Chem., 1999, Vol. 48, pp. 465–476
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THERMODYNAMICS OF COMPLEXATION OF SOME MONOVALENT AND BIVALENT CATIONS BY CROWN ETHERS, BENZO CROWN ETHERS AND CRYPTANDS IN *N*,*N*-DIMETHYLFORMAMIDE

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(Received 6 November 1998)

A complexation study concerning the interaction between Ag^+, NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions with the crown ethers 15-crown-5, benzo-15-crown-5, 18-crown-6, benzo-18-crown-6 and the cryptands (211), (221) and (222) in *N*,*N*-dimethylformamide solution has been carried out at 25°C. The stability constants of the resulting complexes were determined by means of conductometric, calorimetric and potentiometric titrations. The calorimetric titration was also used to determine the reaction enthalpy. It is found that the silver ion forms with cryptands the most stable complexes. Among the investigated alkali and alkaline earth cryptates the $[Li^+\subset 211]$, $[Ca^{2+}\subset 211]$, $[Na^+\subset 221]$, $[Sr^{2+}\subset 221]$, $[K^+\subset 222]$, and $[Ba^{2+}\subset 222]$ cryptates show the highest stability constants. K^+ and Ba^{2+} form with the examined crown ethers the most stable complexes among the alkali and alkaline earth complexes; 15-crown-5 and benzo-15-crown-5 form 2 : 1 complexes with some of the cations.

Keywords: Crown ethers; benzo crown ethers; cryptands; complexes; stability constants; thermodynamic properties

INTRODUCTION

The synthesis of macrocyclic polyethers known as crowns[1] and of macrobicyclic polyethers cryptands,[2] and the observation of their ability to form selective inclusion complexes with a variety of metal ions has led to an extensive study of these ligands and their complexes. Therefore a large

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number of results have been reported during the last years. Most of them can be found in reviews published by Izatt *et al.*[3–5] The stability constants and thermodynamics of complexation of the crown ethers 15-crown-5, benzo-15-crown-5, 18-crown-6, benzo-18-crown-6 and of the cryptands (211), (221) and (222) have mainly been studied with alkali and alkaline earth ions in water and various non-aqueous solvents. There are some additional investigations about the complexation of cryptands with silver(I). However in comparison with numerous literature reports on silver(I), ammonium, alkali and alkaline earth crown ether complexes and cryptates in non-aqueous solvents, systematic investigation of complex formation of the mentioned ions and ligands in the solvent *N*,*N*-dimethylformamide (DMF) has received much less attention. Mainly stability constants have been published.[6–16] Only a few data about reaction enthalpies are available from the literature.[6,15,17] The literature data always concern 1 : 1 complexation.

For a better understanding of the influence of the solvent DMF on complexation the published values are not sufficient. There is need for more information on thermodynamics of 1 : 1 and 2 : 1 complexation reactions. Thus, we systematically studied the 1 : 1 and 2 : 1 complexation of mono and bivalent cations by crown ethers, benzo crown ethers and cryptands in DMF using potentiometric, calorimetric and conductometric methods. Values of stability constants and corresponding thermodynamic parameters of 1 : 1 and 2 : 1 complexations are discussed in detail and compared with data from the literature.

EXPERIMENTAL

The crown ethers 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and the cryptands (211), (221) and (222) (all from Merck) were used without further purification. The chemical structures of these ligands are given in Figure 1. The anhydrous salts used were silver tetrafluoroborate (Merck), ammonium perchlorate (Fluka), lithium perchlorate (Ventron), sodium perchlorate (Ventron) potassium perchlorate (Johnson Matthey), rubidium perchlorate (Johnson Matthey), magnesium perchlorate (Ventron), barium perchlorate (Merck) and sodium tetraphenylborate (Fluka). The hydrous salts calcium perchlorate tetrahydrate (Johnson Matthey) and strontium perchlorate hexahydrate (Johnson Matthey) were dried in DMF solution with molecular sieves. The salts were of the highest purity commercially available and were used without further purification. The tetraphenylborates of NH_4^+, Li^+, K^+, Rb^+,Cs^+, Mg^{2+},

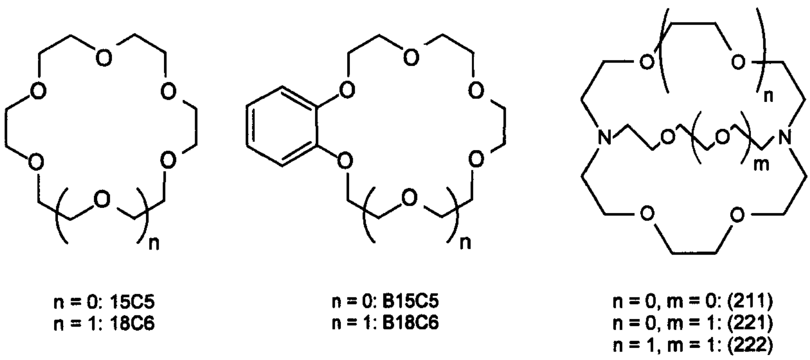

FIGURE 1 Chemical structures of the ligands.

Ca^{2+}, Sr^{2+} and Ba^{2+} were prepared and purified according to published procedures.[18,19] As solvent, DMF (Fluka; $H_2O < 0.01\%$) was used.

During complex formation the following reactions may take place between the cation M^{n+} and the ligand molecule L

$$M^{n+} + L \Leftrightarrow ML^{n+} \tag{1}$$

$$ML^{n+} + L \Leftrightarrow ML_2^{n+}. \tag{2}$$

The correspondent stability constants are given by

$$K_1 = [ML^{n+}]/[M^{n+}][L] \tag{3}$$

and

$$K_2 = [ML_2^{n+}]/[ML^{n+}][L]. \tag{4}$$

The stability constant, K_1 of 1 : 1 complexes of the ligands 18C6, B18C6 and the cryptands with $K < 10^5\,dm^3\,mol^{-1}$ were determined by means of calorimetric titrations. The reaction enthalpies ΔH of all complexation reactions were obtained by calorimetric titrations.

During a calorimetric titration the measured heat, Q, is related to reaction enthalpies by

$$Q = n_1\Delta H_1 + n_2(\Delta H_1 + \Delta H_2), \tag{5}$$

where n_1 and n_2 are the number of moles of 1 : 1 and 2 : 1 complexes formed, respectively. A ligand solution ($8 \times 10^{-2}\,mol\,dm^{-3}$) was titrated continuously into a salt solution ($5 \times 10^{-3}\,\text{mol dm}^{-3}$) to determine the stability constant of the 1 : 1 complexes with $K < 10^5\,\text{dm}^3\,\text{mol}^{-1}$ and their reaction enthalpies. The evaluation of the measured thermograms has already been described in detail.[20–22]

In order to obtain reaction enthalpies of complexes with $K > 10^5\,\text{dm}^3\,\text{mol}^{-1}$ or ΔH_1 values of 1 : 1 complexation if a 2 : 1 complexation is possible a ligand solution ($8 \times 10^{-2}\,\text{mol dm}^{-3}$) was titrated into a solution of the salt (1×10^{-2}–$5 \times 10^{-2}\,\text{mol dm}^{-3}$). Under these conditions the ligand concentration in the reaction vessel is much smaller than the salt concentration. Thus no 2 : 1 complexes should be formed.

To obtain the ΔH_2 values of the 2 : 1 complexation reactions the sum of the reaction enthalpies

$$\Delta H_{\text{ov}} = \Delta H_1 + \Delta H_2 \tag{6}$$

has been determined from a competition reaction for the 2 : 1 complexes with the cryptand Cry (222). A solution of the cryptand ($8 \times 10^{-2}\,\text{mol dm}^{-3}$) was titrated into a solution containing the salt ($5 \times 10^{-2}\,\text{mol dm}^{-3}$) and the ligand ($1 \times 10^{-2}$–$5 \times 10^{-1}\,\text{mol dm}^{-3}$). The following competition reaction takes place

$$\text{ML}_2^{n+} + \text{Cry} \Leftrightarrow \text{MCry}^{n+} + 2\text{L}. \tag{7}$$

Using the separately measured reaction enthalpies, ΔH_{Cry}, for the complexation of the cation with the cryptand (222), ΔH_{ov} can be calculated from

$$\Delta H_{\text{ov}} = \Delta H_{\text{Cry}} - \Delta H' \tag{8}$$

$\Delta H'$ is the enthalpy of the competitive reaction shown in equation (7). Some competitive titrations were performed with different ratios of ligand to salt concentrations to ensure the complete formation of the 2 : 1 complex. According to equation (6) the value of ΔH_2 can easily be calculated by using the separately determined value of ΔH_1. All calorimetric titrations were performed with a Tronac model 450 calorimeter.

To obtain the complex stabilities of the silver cryptates direct potentiometric titrations were performed using a silver-selective electrode (Metrohm EA 282). The experimental set-up and the evaluation of the measured data has already been described in the literature in detail.[23] A solution containing the ligand ($1 \times 10^{-2}\,\text{mol dm}^{-3}$) was titrated into a silver(I) solution ($1 \times 10^{-3}\,\text{mol dm}^{-3}$). The stability constants of the formed ammonium, alkali and alkaline earth cryptates were measured using disproportionate potentiometric titrations with Ag^+.[24] A solution containing the salt (2×10^{-2} mol dm^{-3}) and the ligand (1×10^{-2} mol dm^{-3}) was titrated into a Ag^+ solution (1×10^{-3} mol dm^{-3}). In this case the competition reaction shown in (9) takes place

$$ML^{n+} + Ag^+ \Leftrightarrow AgL^+ + M^{n+} \tag{9}$$

with the corresponding stability constant K'.

$$K' = [AgL^+][M^{n+}]/[ML^{n+}][Ag^+]. \tag{10}$$

The separately measured stability constant of the silver complex, K_{Ag}, enables the calculation of the unknown value K of the formed complex using the measured value K'.

$$K = K_{Ag}/K'. \tag{11}$$

During all potentiometric titrations the ionic strength was kept constant at $I = 5 \times 10^{-2}$ mol dm^{-3} using tetrabutylammonium perchlorate (Fluka) as supporting electrolyte.

The stability constants of the 1 : 1 and 2 : 1 complexes with the ligands 15C5 and B15C5 were determined by conductometric titrations (Metrohm Conductometer 660, cell constant 0.7624 cm^{-1}) at constant salt concentration.[25] A ligand solution (2×10^{-1}–6×10^{-1} mol dm^{-3}) employing the salt solution as solvent was titrated into a salt solution (2×10^{-3} mol dm^{-3}). The observed equivalent conductance Λ_{obs}, can be described by the sum of the equivalent conductances for the cation, Λ_+, the formed 1 : 1 complex, Λ_{c1}, the formed 2 : 1 complex, Λ_{c2}, and the anion, Λ_- as shown in (12).

$$\Lambda_{obs} = \Lambda_+[M^{n+}] + \Lambda_{c1}[ML^{n+}] + \Lambda_{c2}[ML_2^{n+}] + \Lambda_-. \tag{12}$$

The mathematical treatment employed and the evaluation of the obtained curves have already been described in detail.[26]

RESULTS AND DISCUSSION

The values of log K_1, ΔH_1, and $T\Delta S_1$ for the 1 : 1 complexation reactions of mono- and bivalent cations with the crown ethers 15C5, B15C5, 18C6, and B18C6 in DMF are summarized in Table I. For comparison, published data

TABLE I Stability constants K_1 (in dm^3 mol^{-1}) and thermodynamic parameters ΔH_1 and $T\Delta S_1$ (in kJ mol^{-1}) for the complex formation of 1 : 1 complexes of alkali ions, alkaline earth ions, the silver ion and the ammonium ion with different crown ethers in DMF solutions at 25°C

Ion	*Parameter*	*15C5* ($r = 0.9$ Å[a])	*B15C5* ($r = 0.9$ Å[a])	*18C6* ($r = 1.4$ Å[a])	*B18C6* ($r = 1.4$ Å[a])
Ag$^+$ ($r = 1.15$ Å[b])	$\log K_1$	1.80 ± 0.11	1.91 ± 0.14	2.62 ± 0.18	2.71 ± 0.21
	$-\Delta H_1$	18.0 ± 1.3	7.6 ± 0.6	18.1 ± 0.7	17.4 ± 1.1
	$T\Delta S_1$	−7.7 ± 0.7	3.3 ± 0.2	−2.8 ± 0.1	−2.0 ± 0.1
NH$_4^+$ ($r = 1.43$ Å[b])	$\log K_1$	3.23 ± 0.28	1.92 ± 0.23	3.07 ± 0.13 3.07[c]	3.41 ± 0.20
	$-\Delta H_1$	9.5 ± 0.9	5.0 ± 1.0	32.6 ± 0.9 37.3[c]	9.6 ± 0.9
	$T\Delta S_1$	8.9 ± 0.6	5.9 ± 0.1	−15.1 ± 0.2 −19.7[c]	9.8 ± 2.1
Li$^+$ ($r = 0.73$ Å[b])	$\log K_1$	[d]	[d]	2.50 ± 0.10	2.44 ± 0.16
	$-\Delta H_1$	[e]	[e]	0.7 ± 0.5	0.5 ± 0.3
	$T\Delta S_1$			13.6 ± 1.1	13.2 ± 1.4
Na$^+$ ($r = 1.02$ Å[b])	$\log K_1$	2.75 ± 0.13 1.97[f]	1.42 ± 0.25 1.6[f]	2.67 ± 0.13 2.43[c] 2.31[f] 2.4[g] 2.28[h]	2.59 ± 0.11 2.5[i]
	$-\Delta H_1$	18.0 ± 1.2	12.4 ± 1.2	16.4 ± 1.2 22.2[c]	24.4 ± 0.7
	$T\Delta S_1$	−2.3 ± 0.8	−4.3 ± 0.2	−1.2 ± 0.4 −6.6[c]	−9.6 ± 1.3
K$^+$ ($r = 1.38$ Å[b])	$\log K_1$	3.90 ± 0.25	2.87 ± 0.24	4.47 ± 0.38 4.21[c] 4.31[g] 4.01[h]	3.63 ± 0.17 3.31[h] 3.6[i]
	$-\Delta H_1$	24.0 ± 2.0	19.8 ± 0.9	38.1 ± 1.2 38.8[c]	32.6 ± 3.0
	$T\Delta S_1$	−1.7 ± 2.4	−3.5 ± 0.5	−12.6 ± 0.9 −14.8[c]	−11.9 ± 4.0
Rb$^+$ ($r = 1.49$ Å[b])	$\log K_1$	3.73 ± 0.30	2.77 ± 0.25	4.14 ± 0.11 3.92[c] 3.98[g] 3.75[h]	3.46 ± 0.16 3.2[i]
	$-\Delta H_1$	22.5 ± 2.3	16.2 ± 1.4	41.1 ± 2.1 44.6[c]	29.3 ± 2.3
	$T\Delta S_1$	−1.2 ± 1.9	−0.4 ± 0.4	−17.5 ± 2.8 −22.2[c]	−9.5 ± 1.4
Cs$^+$ ($r = 1.70$ Å[b])	$\log K_1$	2.72 ± 0.21 0.91[j]	0.85 ± 0.15	3.62 ± 0.13 3.64[c] 3.67[g] < 4[j]	3.26 ± 0.14 2.8[i]
	$-\Delta H_1$	19.2 ± 0.4	11.2 ± 1.4	48.4 ± 1.2 50.0[c]	27.2 ± 2.0
	$T\Delta S_1$	−3.7 ± 0.8	−6.4 ± 0.5	−27.8 ± 2.0 −29.2[c]	−8.5 ± 2.8
Mg^{2+} ($r = 1.65$ Å[b])	$\log K_1$	[d]	[d] < 2[k]	1.99 ± 0.99 2.50[k]	[d]
	$-\Delta H_1$	[e]	[e]	0.7 ± 0.3	[e]
	$T\Delta S_1$			10.7 ± 0.8	

TABLE I (*Continued*)

Ion	*Parameter*	*15C5* ($r = 0.9$ Å^a)	*B15C5* ($r = 0.9$ Å^a)	*18C6* ($r = 1.4$ Å^a)	*B18C6* ($r = 1.4$ Å^a)
Ca^{2+} ($r = 1.00$ Å^b)	$\log K_1$	^{d}	^{d} 2.32^k	2.58 ± 0.12 3.03^k	2.50 ± 0.10
	$-\Delta H_1$	^{e}	^{e}	1.9 ± 0.9	15.7 ± 1.0
	$T\Delta S_1$			12.8 ± 0.2	-1.5 ± 0.5
Sr^{2+} ($r = 1.16$ Å^b)	$\log K_1$	0.50 ± 0.10	^{d} 2.15^k	2.51 ± 0.91 4.23^k	2.64 ± 0.14
	$-\Delta H_1$	6.2 ± 1.0	1.3 ± 0.5	9.6 ± 2.1	15.7 ± 0.1
	$T\Delta S_1$	-3.4 ± 0.4		4.7 ± 1.0	-0.6 ± 0.5
Ba^{2+} ($r = 1.36$ Å^b)	$\log K_1$	1.26 ± 0.18	^{d}	3.75 ± 0.15 5.29^k	2.68 ± 0.12
	$-\Delta H_1$	11.5 ± 1.1	4.5 ± 1.2	43.3 ± 2.9	23.4 ± 2.0
	$T\Delta S_1$	-4.3 ± 0.1		-21.9 ± 2.0	-8.1 ± 2.7

[a] Ref. [27]. [b] Ref. [28]. [c] Ref. [6]. [d] Measured conductance too small for calculation. [e] Heat produced during titration too small for calculation. [f] Ref. [7]. [g] Ref. [8]. [h] Ref. [9]. [i] Ref. [10]. [j] Ref. [11]. [k] Ref. [12].

are included.[6–12] Concerning the monovalent cations the published data are in a good agreement with the experimental values except for the data for the complexation of Na^+ and Cs^+ by 15C5.[7,11] This may be explained by the fact that the authors only considered the formation of 1 : 1 but not of 2 : 1 complexes. The literature data for the complexation of the alkaline earth ions by B15C5 and 18C6 could not be confirmed.[12]

The stabilities of the alkali and alkaline earth ion complexes are influenced by the cavity size to ionic size ratio and solvation effects. This can easily be seen for K^+ and Ba^{2+} which form the most stable complexes. The better the ion fits into the cavity the stronger generally are the interactions between the complexed ion and all donor atoms of the ligand. This show the ΔH_1 values of the investigated alkali complexes of 15C5, B15C5, B18C6 and all alkaline earth complexes. On the other hand, the ΔH_1 values of the 18C6 alkali complexes increase with increasing alkali ionic radii. This can be explained by the decreased solvation of the ions with increasing ionic size.

Concerning the benzo substituted crown ethers B15C5 and B18C6, the benzo group reduces the basicity of the two oxygen atoms next to it, the flexibility of the molecule and the cavity size. Thus, in comparison to the corresponding unsubtituted crown ether complexes the stability constants of the B15C5 and B18C6 complexes and the reaction enthalpies of the complex formation decrease. Exceptions are the data for complexation of Li^+, Na^+, Ca^{2+} and Sr^{2+} by B18C6. These complexes show nearly the same stability constants as the corresponding 18C6 complexes. The sodium, calcium and strontium ions are smaller than the cavities of 18C6 and B18C6. Considering the decreasing cavity size from 18C6 to B18C6, these ions are allowed to form interactions with more donor atoms, which can be seen in the enthalpies. The lithium ion is much smaller than the cavity size of the ligands 18C6 and B18C6. Therefore the lithium ion interacts only with some donor atoms of both ligands. Thus no changes of stabilities and enthalpies of the complexation reaction comparing 18C6 and B18C6 could be observed.

In spite of strong solvation in DMF silver(I) forms complexes with all crown ethers. Due to its size and charge, the ammonium ion shows complexation behaviour like the alkali ions.

If one cation is too big to fit into the cavity of the ligand, a 2 : 1 complex could be formed.[27,28] In the present work there is no evidence for a 2 : 1 complex formation between the investigated ions and the crown ethers 18C6 and B18C6 in DMF. Even with the cesium ion no 2 : 1 complexation was observed with 18C6 and B18C6. The results for 2 : 1 complex formation of the crown ethers 15C5 and B15C5 with mono and bivalent cations are summarized in Table II.

The stability constants K_1 concerning the 1 : 1 complexation are always higher compared to the stability constants, K_2, of the 2 : 1 complexation. However, values of the reaction enthalpies, ΔH_1 and ΔH_2, show quite different behaviour. If the complexed ion fits well into the cavity of the first ligand molecule, small interactions with a further ligand molecule take place and ΔH_2 is smaller compared to ΔH_1. Bigger ions which do not fit well into the cavity of the first ligand molecule interact more strongly with the second ligand molecule. This is due to the weakening of the interactions between the solvent molecules and the ion by the first ligand. Thus, during the 2 : 1 complexation the second ligand is able to release these solvent molecules without requiring much energy. As a result the values of ΔH_2 of the 2 : 1 complexation are higher compared to the values of the 1 : 1 complexation. If the complexed ion is so big that both ligands of the 2 : 1 complex do not influence each other, the obtained reaction enthalpies ΔH_1 and ΔH_2 are nearly equal.

In Table III obtained values concerning the complexation of different monovalent and bivalent cations by the cryptands (211), (221) and (222) in DMF solutions are summarized. With few exceptions the obtained values are almost identical compared to values reported in literature.[13–17] The reaction enthalpies of the complexation reactions of Ag^+ with (211) and Cs^+ with (222) differ from reported data.[15] The values published in the literature had been deterined indirectly from the temperature dependence of the stability constants. Thus, the accuracy of these values is not as hig as the measurements by calorimetric titrations.[30] There is also a difference between

TABLE II Stability constants K_2 (in dm^{3}mol^{-1}) and thermodynamic parameters ΔH_2 and $T\Delta S_2$ (in kJ mol^{-1}) for the complex formation of 2 : 1 complexes of alkali ions, alkaline earth ions, the silver ion and the ammonium ion with the crown ethers 15-crown-5 and benzo-15-crown-5 at 25°C in DMF solutions

Ion	*Parameter*	*15C5* ($r = 0.9$ Å^a)	*B15C5* ($r = 0.9$ Å^a)
Ag$^+$	$\log K_2$	0.50 ± 0.30	c
($r = 1.15$ Å^b)	$-\Delta H_2$	-2.9 ± 1.3	d
	$T\Delta S_2$	0 ± 0.7	
NH_4^+	$\log K_2$	0.59 ± 0.02	0.32 ± 0.10
($r = 1.43$ Å^b)	$-\Delta H_2$	24.0 ± 0.9	16.3 ± 1.0
	$T\Delta S_2$	-23.7 ± 0.8	-14.5 ± 0.4
Li$^+$	$\log K_2$	c	c
($r = 0.73$ Å^b)	$-\Delta H_2$	d	d
	$T\Delta S_2$		
Na$^+$	$\log K_2$	1.21 ± 0.20	0.75 ± 0.25
($r = 1.02$ Å^b)	$-\Delta H_2$	3.9 ± 1.2	5.0 ± 1.2
	$T\Delta S_2$	3.0 ± 0.7	0.7 ± 0.2
K$^+$	$\log K_2$	1.65 ± 0.10	1.24 ± 0.16
($r = 1.38$ Å^b)	$-\Delta H_2$	27.7 ± 2.0	27.3 ± 0.9
	$T\Delta S_2$	-18.2 ± 1.9	-20.4 ± 0.2
Rb$^+$	$\log K_2$	1.57 ± 0.17	1.02 ± 0.2
($r = 1.49$ Å^b)	$-\Delta H_2$	28.7 ± 2.3	24.8 ± 1.4
	$T\Delta S_2$	-19.7 ± 1.1	-19.0 ± 0.2
Cs$^+$	$\log K_2$	1.11 ± 0.15	c
($r = 1.70$ Å^b)	$-\Delta H_2$	18.5 ± 2.7	9.8 ± 2.4
	$T\Delta S_2$	-12.4 ± 1.8	
Mg^{2+}	$\log K_2$	c	c
($r = 0.65$ Å^b)	$-\Delta H_2$	d	d
	$T\Delta S_2$		
Ca^{2+}	$\log K_2$	c	c
($r = 1.00$ Å^b)	$-\Delta H_2$	d	d
	$T\Delta S_2$		
Sr^{2+}	$\log K_2$	c	c
($r = 1.16$ Å^b)	$-\Delta H_2$	3.1 ± 1.0	d
	$T\Delta S_2$		
Ba^{2+}	$\log K_2$	0.15 ± 0.08	c
($r = 1.36$ Å^b)	$-\Delta H_2$	3.8 ± 1.1	d
	$T\Delta S_2$	-2.9 ± 0.2	

[a] Ref. [27]. [b] Ref. [28]. [c] Measured conductance too small for calculation. [d] Heat produced during titration too small for calculation.

the published and the measured value of the stability constant of the cryptate [Ca^{2+}$\subset$211].[14,16] The obtained value was determined by means of potentiometric titration and confirmed by an independent investigation using calorimetric titration. The complex stability for the complexation of K$^+$ by (211) could not be determined.[13,14]

The interpretation of the results for the complexation behaviour of the crown ethers given above is also valid for the cryptands. Thus, the complex

TABLE III Stability constants K (in $dm^3 mol^{-1}$) and thermodynamic parameters ΔH and $T\Delta S$ (in $kJ mol^{-1}$) for the complexation of alkali ions, alkaline earth ions, the silver ion and the ammonium ion with cryptands in DMF solutions at 25°C

Ion	*Parameter*	(211) (r = 0.8 Å[a])	(211) (r = 1.1 Å[a])	(222) (r = 1.4 Å[a])
Ag^+ (r = 1.15 Å[b])	log K	8.55 ± 0.05 8.62[c]	12.53 ± 0.03 12.41[c] 12.43[d]	10.00 ± 0.02 10.07[c] 10.03[d]
	$-\Delta H$	59.6 ± 1.6 98.5[d]	85.2 ± 1.5 88.7[d]	68.1 ± 1.3 56.4[d] 65.6[e]
	$T\Delta S$	− 10.8 ± 1.3	− 13.67 ± 1.3	− 11.0 ± 1.4
NH_4^+ (r = 1.43 Å[b])	log K	[f]	5.13 ± 0.05	0.45 ± 0.05
	$-\Delta H$	[g]	46.3 ± 1.4	61.0 ± 1.1
	$T\Delta S$		− 17.0 ± 1.7	− 24.1 ± 1.4
Li^+ (r = 0.73 Å[b])	log K	6.66 ± 0.03 6.99[c]	3.48 ± 0.04 3.58[c] 3.52 ± 0.12[h]	[f] [g]
	$-\Delta H$	38.0 ± 1.2	15.4 ± 1.3	
	$T\Delta S$	0.0 ± 1.2	4.5 ± 1.0	
Na^+ (r = 1.02 Å[b])	log K	4.85 ± 0.02 5.23[c] 4.73 ± 0.16[f] 5.17[i]	7.80 ± 0.05 7.93[c] 7.86[i]	5.93 ± 0.03 6.17[c]
	$-\Delta H$	35.7 ± 1.2	50.9 ± 2.0	43.6 ± 1.1 40.0[e]
	$T\Delta S$	− 8.0 ± 1.3	− 6.3 ± 0.3	− 9.7 ± 1.2
K^+ (r = 1.38 Å[b])	log K	< 2.5[c] [f] 1.51[i]	6.71 ± 0.05 6.66[c] 6.59[i]	7.82 ± 0.05 7.98[c] 7.89[d] 8.03[i]
	$-\Delta H$	3.4 ± 1.0	53.5 ± 1.8	60.2 ± 1.3 53.0[d] 54.5[e]
	$T\Delta S$		− 15.2 ± 1.3	− 15.6 ± 1.1
Rb^+ (r = 1.49 Å[b])	log K	[f]	5.19 ± 0.03 5.35[c]	6.43 ± 0.04 6.78[c]
	$-\Delta H$	0.9 ± 0.3	50.2 ± 2.0	59.3 ± 1.1 55.0[e]
	$T\Delta S$		− 20.6 ± 1.8	− 22.6 ± 1.4
Cs^+ (r = 1.70 Å[b])	log K	[f]	3.5 ± 0.05 3.61[c]	2.13 ± 0.05 2.16[c]
	$-\Delta H$	[g]	3.38 ± 0.24[h] 36.6 ± 1.9	11.2 ± 0.4 40.0[e]
	$T\Delta S$		− 16.6 ± 1.7	0.9 ± 0.9
Mg^{2+} (r = 1.65 Å[b])	log K	[f]	[f]	[f]
	$-\Delta H$	[g]	[g]	[g]
	$T\Delta S$			
Ca^{2+} (r = 1.00 Å[b])	log K	1.54 ± 0.03 3.08[c] 1.64 ± 0.17[h] 3.09[j]	5.81 ± 0.03 6.67[c] 6.58[j]	3.16 ± 0.03 3.84[c] 3.16 ± 0.18[i] 3.79[j]
	$-\Delta H$	21.2 ± 0.7	38.5 ± 1.2	17.0 ± 0.8
	$T\Delta S$	− 12.4 ± 0.8	− 5.3 ± 1.3	1.0 ± 0.5

TABLE III (*Continued*)

Ion	*Parameter*	(211) ($r = 0.8$ Å[a])	(211) ($r = 1.1$ Å[a])	(222) ($r = 1.4$ Å[a])
Sr^{2+}	$\log K$	[f]	7.39 ± 0.04	6.99 ± 0.02
($r = 1.16$ Å[b])			7.95[j]	7.30[j]
	$-\Delta H$	1.0 ± 0.5	51.8 ± 1.3	44.6 ± 1.5
	$T\Delta S$		-9.6 ± 1.5	-4.7 ± 1.4
Ba^{2+}	$\log K$	[f]	6.60 ± 0.05	8.01 ± 0.03
($r = 1.36$ Å[b])			6.60[i]	7.70[i]
			6.96[j]	8.39[j]
	$-\Delta H$	[g]	40.3 ± 1.2	54.8 ± 1.3
	$T\Delta S$		-2.6 ± 1.5	-9.1 ± 1.5

[a]Ref. [29]. [b]Ref. [28]. [c]Ref. [14]. [d]Ref. [15]. [e]Ref. [16]. [f]Measured potential too small for calculation. [g]Heat produced during titration too small for calculation. [h]Calorimetric titration. [i]Ref. [13]. [j]Ref. [17].

stabilities of the investigated alkali and alkaline earth cryptates show the characteristic dependency of "hole size selectivity". No 2:1 complexation could be observed. The stability constants of the cryptates are several orders of magnitude higher compared to the crown ether complexes, caused by the bicyclic structure of the cryptands. These cryptands shield the complexed cations more efficiently from the surrounding solvent.

Silver cryptates show the highest complex stabilities among the formed cryptates. According to the HSAB model of Pearson both the silver ion and the nitrogen atoms of the cryptands are soft.[31] Therefore the nitrogen atoms show much stronger interactions with the silver ion compared to the hard alkali and alkaline ions. This can easily be seen with the high reaction enthalpies.

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